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THE DYEING OF NATURAL COTTON WITH DIRECT DYES: A DETERMINATION OF THE HEAT OF DYEING[1]

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Abstract

The equilibrium sorption of a purified direct dye on natural cotton yarn has been determined over a range of dye-bath concentrations (20 to 175 mgm. of dye per litre of solution) and temperatures (75° to 90° C.). The liquor-to-yarn ratio in the dye bath, which contained sodium chloride (4.00 gm. per litre), was sufficiently high to permit the concentration of dye in solution to remain essentially constant throughout a dyeing experiment. The dye was removed from the skeins using a pyridine–ethanol–water solution, and the concentration of dye in the latter determined spectrophotometrically.

Differential heats of dyeing may be calculated from the results obtained. For an equilibrium sorption of 475 mgm. of Calcodur Blue 4GL per 100 gm. of natural cotton yarn, the value of 15 kgm-cal. per mole was found, and it is shown that the differential heat of dyeing increases as the value of the equilibrium sorption decreases. The results are interpreted in the light of the modern view of the structure of cellulose.

Introduction

In a relatively recent publication from this laboratory (7) reporting a study of the dyeing of natural cotton with direct dyes, reference was made to review papers dealing with the dyeing of cellulose with direct dyes and to other recent papers concerned with this subject, and, in particular, the interaction of direct dyes and cotton. Since this earlier paper was written, a number of significant contributions to our knowledge of the direct dyeing of cellulosic materials have appeared. Of these there may be mentioned the discussion of the physical chemistry of dyeing by Valko (28, pp. 594-619), the paper by Standing, Warwicker, and Willis (25) in which the direct dyeing process is assumed to be essentially one of diffusion in the cellulose and in which a diffusion–adsorption equation is developed and its validity tested by applying it to experimental data published by Neale and his collaborators; the paper by Morton (12) in which a molecular theory of the dyeing of cellulose with substantive dyes is presented; and that by Lemin, Vickers, and Vickerstaff

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(9) (a paper that gave rise to published discussion (1, 29)) in which the results of a study of the rate of dyeing of numerous direct dyes, including binary combinations, on cotton are presented as well as other studies leading to a proposed classification of direct dyes from the point of view of practical application. The report of the committee appointed in 1944 by the Council of the Society of Dyers and Colourists to discuss the dyeing properties of direct cotton dyes was published some months ago (5). Other recent papers concerned with the interaction of direct dyes and cellulose are those by Rose (22), Neale (14), Brass and Schreier (3), and Wälchli (30).

Direct cotton dyes have been known for over sixty years (31), but our understanding of their action is still very inadequate. In the last 15 years an appreciable number of careful studies of the dyeing of cellulosic materials by direct dyes have been carried out, but to date very little attention appears to have been given to the energetics of the process. The authors are aware of only two published determinations of the heat of dyeing of direct dyes on cellulose (11, p. 274; 32); both of these determinations were made using viscose sheet. In the present investigation a number of isotherms for the sorption of a purified blue direct dye on natural cotton yarn were determined. From these data, values for the heat of dyeing have been calculated and an attempt has been made to interpret their variation with the extent of equilibrium sorption.

Materials and Methods

Cotton

Natural cotton yarn from the same batch as that used in an earlier study (7) was the sorbent; the yarn was 1/4's count wound in 14 oz. packages on Franklin springs.

The cotton was wound by hand into small skeins (weighing slightly more than 0.2 gm.) and then dried, weighed, etc., by the procedure described before (7) to give a skein weighing, in the present study, 0.2000 ± 0.0005 gm. on a dry basis. Before being dyed, the weighed dry skein was allowed to stand in air for some hours.

Dyestuff

The trisazo direct dye Calcodur Blue 4GL (Colour Index 533), after purification, was used throughout the present study. The method of purification, based on that recommended by Rose (21), was a slight modification of that used in the earlier study (7). The essential differences were that the precipitate produced by the interaction of the dye with di-*o*-tolylguanidine was washed with a very dilute solution of di-*o*-tolylguanidine hydrochloride rather than with distilled water (to decrease the tendency of the precipitate toward peptization); that the regenerated dye was washed with isopropanol (99%) rather than with methanol; and that before use the ground dye was dried for 24 hr. ***in vacuo*** at 110° C. over phosphorus pentoxide—this procedure served to remove residual di-*o*-tolylguanidine from the dyestuff.

Dyeing Apparatus

The dye pots consisted of short-necked round-bottomed Pyrex boiling flasks of three litres' capacity to which were attached, by means of a rubber stopper, water-cooled condensers. The cotton yarn to be dyed was attached to a Pyrex glass skein holder (loosely, by means of platinum wires), which also served as a stirrer. The glass shaft of the stirrer passed up through the condenser and was given an up-and-down motion (two cycles per second) by an electromagnetic device similar in principle to the one described by Tulk and Seagers (26) but with the following modification, which resulted in more uniform operation: the pendulum was removed and there was substituted a wooden wheel (driven by a constant speed induction motor) carrying a semi-circular phosphor bronze strip. Two fixed phosphor bronze brushes, which were in series with the electromagnetic stirring motors, pressed on this strip; thus, as the wheel revolved, the circuit was alternately closed and opened in very regular cycles.

The dye pots were immersed in a constant temperature bath constructed so as to permit a temperature control of $\pm$ 0.1° C. in the range 70° to 97° C. Temperatures reported in this paper are corrected for exposed stem, and were determined using a thermometer that had been compared with one newly calibrated in the Division of Physics of the National Research Council of Canada.

Dyeing Procedure

In all dyeing experiments reported in this paper, 0.2000 $\pm$ 0.0005 gm. (dry weight) of natural cotton yarn was dyed using 2900 ml. of dye-bath solution containing 4.00 gm. per litre of sodium chloride (analyzed grade); the liquor-to-yarn ratio was thus 14,500 : 1. The dye bath contained dye at a concentration ranging from 20 to 176 mgm. per litre (2.3×10^{-5} to 2.0×10^{-4} *M*). These conditions, which are of course far removed from those used in commercial dyeing, permitted equilibrium dyeing to be attained at the temperatures employed in a reasonable length of time (12 to 48 hr.) without any significant change occurring in the concentration of dye in the dye bath (in all experiments, the exhaustion at equilibrium was less than 1.1%).

The dye solution was placed in a dye pot, which, with condenser attached, was preheated over a burner and then was immersed in the thermostat for a period of one hour (to permit thermal equilibrium to be established) before the cotton skein and stirrer were inserted and the dyeing experiment begun. Dyeing was allowed to proceed, under constant temperature conditions, for an appropriate length of time (which, in all experiments except those concerned with rate of dyeing, was until equilibrium sorption had been attained) and then the skein was removed from the dyeing apparatus; it was squeezed dry, rinsed twice in 0.4% sodium chloride solution, again squeezed dry by hand, and then placed in the stripping apparatus (*vide infra*) for removal of the dye. Each rinsing solution consisted of 100 ml. of the sodium chloride solution. No color could be detected visually after rinsing. Because a

concentration of this dye as low as 0.05 mgm. per litre can be detected visually, there was less than 0.01 mgm. of dye removed in the rinsing operation (which was designed to eliminate entrained dye liquor). On the other hand, analysis showed the 0.2 gm. cotton skeins to contain from 0.39 to 1.00 mgm. of dye.

The used dye-bath solution was filtered through a fritted glass disk in order to ascertain whether any appreciable amount of cotton had become separated from the skein. If such was the case, the run was discarded; this occurred in about 5% of the experiments.

Analytical Procedures

A number of workers (e.g., 2, 3, 9, 15) have used pyridine (usually 15 to 25% aqueous) to remove direct dyes from cellulosic material prior to colorimetric determination; this stripping technique was developed from some

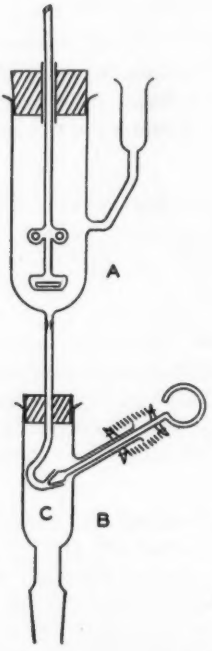

FIG. 1. *Apparatus for removing dyestuff from the dyed skein.*

observations made by Ratelade and Chetvergov (19). Investigations in this laboratory have shown that, at least in the cases of Calcodur Blue 4GL, a solution consisting (by volume) of 25% pyridine (reagent grade), 10% ethanol (95%), and 65% distilled water permitted a significantly faster rate

of dye stripping (at room temperature) than did a 25% pyridine in water solution and, moreover, spectrophotometric tests showed the dye was more stable in the pyridine–ethanol–water solution than in one without alcohol.

The dyed skeins were stripped using the apparatus shown in Fig. 1. The dyed cotton skein was attached (loosely, by means of platinum wires) to the stirrer in the upper chamber. After closing the plunger-operated ground-glass joint at *C*, sufficient stripping solution was introduced through the side arm at *A* to cover the cotton skein, and the stirrer carrying the latter was rotated by an electric stirring motor (not shown). At the end of one hour, the solution was drained from the skein by opening the joint at *C* and allowing the solution to drain through chamber *B* into a 250 ml. volumetric flask (not shown) connected to *B* by a ground glass connection. Fresh stripping solution was introduced, stripping allowed to continue for a further period of six hours, the solution drained again, and a third stripping action allowed to continue for 16 hr., or overnight. The cotton was then rinsed with the stripping solution and the liquid in the volumetric flask made up to volume with the stripping solution. All stripping operations were carried out at room temperature.

A portion of the dye solution from the volumetric flask was placed in a cuvette and the transmittance of the solution measured, at 600 mμ, using a Coleman Model 11 Universal Spectrophotometer fitted with the 'PC-4' filter. Matched rectangular cuvettes, with a path length of 10 mm. were employed; the reference cuvette contained pure stripping solution. From the measured transmittance, the amount of dye originally on the fibre could be calculated,

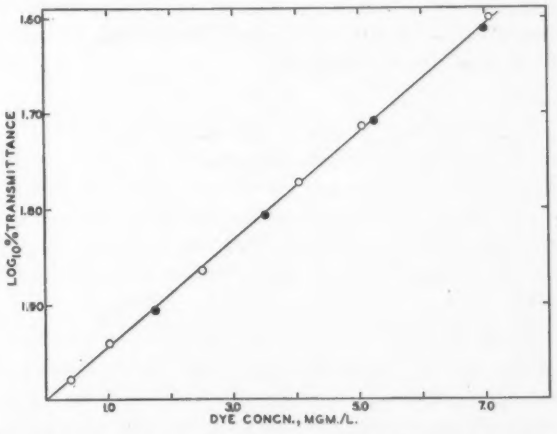

FIG. 2. *Calibration curve (two separate determinations) for the colorimetric determination of dye using the spectrophotometer at a wave length setting of 600 mμ.*

making use of a calibration curve (Fig. 2) constructed from data obtained using solutions of known concentration of dye dissolved in the pyridine–ethanol–water stripping medium.

Experimental Results

Rate of Dyeing

A number of rate of dyeing experiments were carried out in order to ascertain the time required to reach equilibrium sorption under the conditions being used to obtain the sorption isothermal data reported below. Examples of the type of rate curves obtained are shown in Fig. 3. This and other related data,

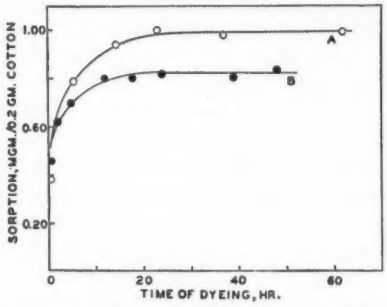

FIG. 3. *Typical rate of sorption curves. Both are for dyeings at 90° C.; the concentration of dye in the bath in Curve A was 200 mgm. per litre of solution, and in Curve B it was 100 mgm. per litre.*

together with the knowledge that the time required to reach equilibrium decreases (at constant temperature) as the concentration of dye in the dye bath decreases, and decreases (at constant dye-bath concentration) as the temperature increases (7), permitted the choice, in the sorption experiments hereinafter described, of dyeing times sufficiently long to have ensured the establishment of equilibrium conditions.

Sorption Isotherms

Three sorption isotherms, at the temperatures 74.4°, 82.4°, and 89.3° C. were determined using the techniques described above. One of these isotherms is shown in Fig. 4, and all three are shown on a log–log plot in Fig. 5. Since the extent of the exhaustion of the dye bath is negligible (less than 1.1% in all cases) the abscissa is the logarithm of either the initial or the equilibrium dye concentration. The experimental data used to construct these curves are given in Table I.

Heat of Sorption (or Dyeing)

If we consider the reaction illustrated by the equation: cellulose – dye sorption complex = cellulose + dye (in solution), and note that the sorbed dye represents a condensed phase of the dye, we may with some justification apply to the system the equation:

$$\frac{d \ln C}{dT} = \frac{\triangle H_d}{RT^2} \text{ or } \frac{d \ln C}{d(1/T)} = \frac{\triangle H_d}{R}$$

where T, the temperature, is in degrees absolute, C is the equilibrium concentration of dye in solution, $\triangle H_d$ is the heat absorbed in the transition from one

phase to another (in this case, desorption) in calories per mole of dye if R, the gas constant, is expressed in calories per mole.

If, then, $\triangle H_d$ may be assumed to be independent of temperature (and such may be expected over a small temperature range) a plot of $\log_{10}C$ (for a fixed

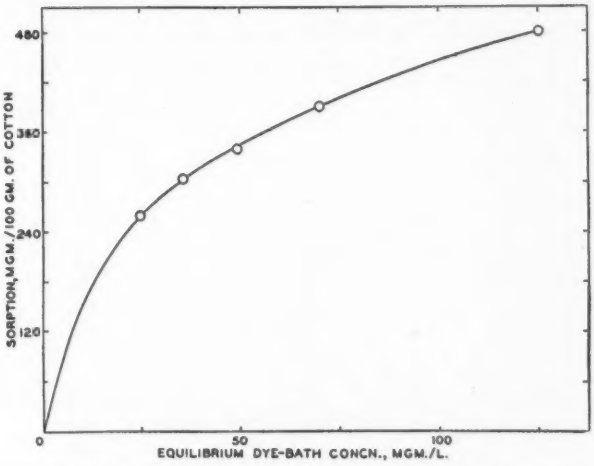

FIG. 4. *Sorption isotherm for a dyeing at 82.4° C.*

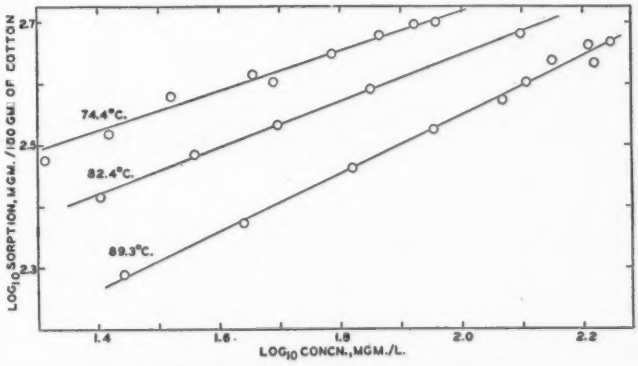

FIG. 5. *Log–log plots of sorption isotherms.*

value of sorption) against $1/T$ should yield a straight line, the slope of which is $-\dfrac{\triangle H_d}{2.303\,R}$. Such plots, for various values of the sorption, are shown in Fig. 6, which was constructed from data obtained using Fig. 5. The slopes of the lines are negative, which means that $\triangle H_d$ is positive (or heat is absorbed) in the desorption reaction; the sorption reaction is exothermic.

The values for the heats of sorption (or dyeing) calculated by this method are given in Table II. The heat of dyeing is $-\triangle H_s$, which is equal to $\triangle H_d$.

TABLE I

EQUILIBRIUM SORPTION AS A FUNCTION OF TEMPERATURE AND CONCENTRATION OF DYE IN THE DYE BATH

Temperature of dyeing, ° C.	Concentration of dye in the bath, mgm./litre	Dye sorbed on the cotton, mgm./100 gm.
	27.8	195
	43.6	235
	66.0	290
	90.0	335
89.3	116.6	375
	127.9	400
	141.2	435
	162.3	460
	165.5	430
	176.6	465
	25.3	260
	36.1	305
82.4	49.8	340
	70.8	390
	125.4	480
	20.5	300
	26.2	330
	33.2	380
74.4	45.2	410
	49.0	400
	61.1	445
	73.3	475
	83.6	495
	90.6	500
67.4	25.2	380
	25.3	385

TABLE II

HEAT OF DYEING AT VARIOUS VALUES OF EQUILIBRIUM SORPTION

Sorption, mgm. dye per 100 gm. cotton	Heat of dyeing ($-\triangle H_s$), kgm-cal. per mole of dye sorbed
473	15.2
422	17.1
383	18.8
355	20.3
316	22.4

Effect of Temperature on Sorption

The data of Table I, and the graphs drawn in Fig. 5 using these data, permit the drawing of some curves illustrating the relation between the

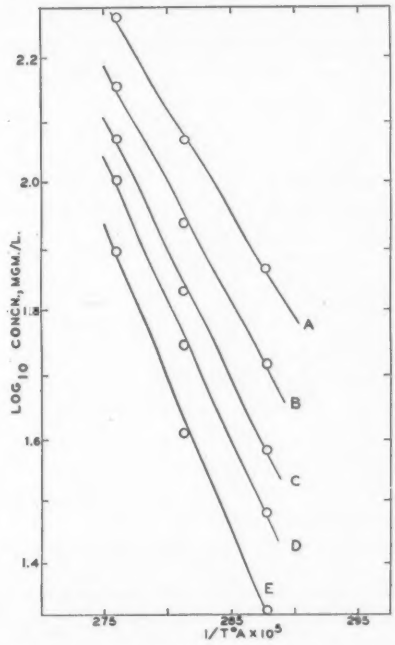

FIG. 6. *'Isosteric' plot relating the equilibrium concentration of dye in the bath to the temperature, at constant values of the equilibrium sorption. The sorption values, in mgm. of dye per 100 gm. of yarn, are: Curve A, 473; Curve B, 422; Curve C, 383; Curve D, 355; Curve E, 316.*

amount of dye sorbed at equilibrium and the temperature of dyeing, under conditions of constant concentration of dye and sodium chloride in the dye bath. These curves are shown in Fig. 7.

Discussion

The rate of dyeing curves (Fig. 3) are of the type to be expected, and it is not surprising that the sorption isotherms (data of Table I) may be fitted by a Freundlich type equation, as is evidenced by the linearity of the log–log plot in Fig. 5. (The data will not, incidentally, fit the Langmuir sorption isotherm equation.) It may be noted that the forms of the rate of sorption curves and of the sorption isotherms obtained in the present experiments where the exhaustion of the dye bath at equilibrium varied from 0.2 to 1.1% are the same as those obtained in earlier work (7) using the same dye and sorbent, but under conditions such that the dye-bath exhaustion was over 90%.

It should be pointed out that the lines in Fig. 5 are not parallel; the slopes vary from 0.32 at a temperature of 74.4° C. to 0.47 at 89.3° C. The value of the equilibrium sorption always increases with increasing residual dye-bath concentration, but the degree of increase decreases as the temperature

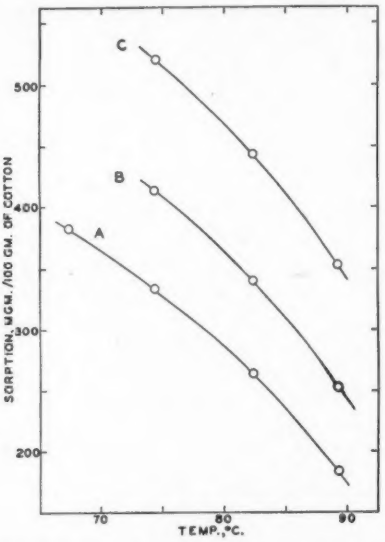

FIG. 7. *'Isobaric' plot relating the equilibrium sorption of dye to the temperature, at constant values for the equilibrium concentration of dye in the bath. The dye-bath concentrations, in mgm. of dye per litre of solution, are: Curve A, 25.2; Curve B, 50.1; Curve C, 100.0.*

decreases. This same effect can be seen in the data of Willis *et al.* (32) for the sorption of Chrysophenine G on viscose sheet in the plot of the isotherms they obtained under conditions, as in the present work, of a fixed concentration of sodium chloride.

It will be noted that the best line drawn through the points in Fig. 6 would show a very slight curvature, rather than being linear as drawn. The slight curvature (if real) may be due to a possible change in the structure of the cotton with changing temperature. It has been pointed out (24) that this consideration requires that care be exercised in deducing the heat of dyeing from the temperature coefficient of the equilibrium sorption. It should also be borne in mind in work of the present type that the sorption values recorded include the mass of any dye that may be present in entrained dye liquor.

The heat of sorption or heat of dyeing values determined by the method yielding the values recorded in Table II are differential heats of sorption (4, p. 26; 10, p. 400), and it is evident that the values increase significantly as the extent of equilibrium sorption decreases. A consideration of the structure of cellulose is helpful in seeking an interpretation of this phenomenon.

It is generally considered that cellulose fibres are composed of crystallites in which the cellulose chains are closely packed together with amorphous intercrystalline regions where the packing of the chains is less regular and their orientation is irregular (17; 23, pp. 203-252; 24). 'Amorphous' is not used here in the sense of a complete lack of geometrical order, but rather to indicate matter that causes a general fogging in the X-ray diagram rather than giving rise to definite diffraction lines. Experiments have indicated that when water molecules are sorbed by cellulose they are able to penetrate the intercrystalline or intermicellar regions, but they are not able to penetrate the crystallites (24; 27, pp. 412-414; 28, pp. 595-596); there is direct evidence that in the sorption of direct dyes by cellulose, the dyes, likewise, do not enter the crystallized regions (28, p. 612). It is to be expected that because cellulose is not homogeneous, its sorption affinity for a particular dye will not be uniform over all the surface with which the dye may come into contact. It is reasonable to suppose that the heats of sorption associated with the different portions of the surface will vary, and, moreover, that the most active (in the sense of sorption affinity for the dye) portions of the surface will be the first to be covered with dye.* This interpretation accounts, qualitatively, for the results found in this work, i.e., that the higher values of the heat of dyeing (or sorption) are associated with the lower values of the equilibrium sorption. (There may also occur multilayer dye sorption where the energy released in the sorbate–sorbate interactions is less than that released, in the earlier stages of sorption, due to sorbate–sorbent interactions.) A variation of the heat of sorption with the amount of sorption is commonly encountered in the study of the sorption of gases and vapors on solids (4, pp. 215-229, 246-253; 10, pp. 405-422). In such systems, ordinarily (although not always (4, pp. 251-262; 8)) the differential heats of sorption decrease with increasing amounts of gas sorbed (4, pp. 26, 247); this variation in the heat of sorption is generally attributed to interactions between sorbed particles, or to nonuniformity of the surface of the sorbent as a result of the surface atoms being separated by varying distances or arranged in differing geometrical configurations (which lead to different interaction energies with the same sorbate molecule) or to the presence of crevices, pockets, etc., in which the heats of sorption are different from those on a plane surface (4, pp. 261-262).

Calculations using the data of Willis *et al.* (32), who studied the sorption of a direct dye on viscose sheet, show that the heat of dyeing decreased with decreasing concentration of sodium chloride in the dye bath (for a given value of the equilibrium sorption), and, as was found in the present work, that the heat of dyeing decreased with increasing values of the equilibrium sorption (for a constant value of the sodium chloride concentration). Using Chrysophenine G (Colour Index 365), Willis *et al.* (32) found values of the heat of dyeing varying from 9.3 to 15.9 kgm-cal. per mole. Meyer has calculated

* *In this connection it is interesting to note that in stripping experiments it was found that most of the dye was removed in two hours, but that over 20 hr. was required to reduce the dye left in the skeins to a trace. Many additional hours of stripping action failed to remove the last trace of dye; this portion was evidently very strongly bonded to the cotton.*

(11, p. 274), from data of Garvie, Griffiths, and Neale (6) a value of 5 kgm-cal. per mole for the heat of dyeing in the case of Chlorazol Fast Red K (Colour Index 278) on viscose sheet, but the present authors do not accept this value. We are not satisfied that the data available permit a calculation of the heat of dyeing in this case. These and other workers have postulated that the sorption of direct dyes on cellulose is due to hydrogen bond formation, and have suggested that the values found for the heat of dyeing lend support to this view. The present authors do not feel that values for the heat of dyeing can, *per se*, be of much, if any, help in supporting the hydrogen bonding theory because of the complexity of the situation: one cannot consider that the average direct dye is necessarily bound to the cellulose by only one hydrogen bond,* and even if this were possible, the energy associated with the formation of a hydrogen bond is, according to Pauling (18, p. 333), in general from 4 to 8 kgm-cal. per mole depending upon the atoms bonded and on the substance in which the bonding occurs. The hydrogen bond is thus a relatively weak bond (18, p. 284; 20, p. 146). Valko has pointed out (28, pp. 606-607) that although hydrogen bonding may well be an important factor in accounting for the interaction between dye and fibre, there are other types of forces to be considered.

It has been stated (24) that the temperature coefficient of the equilibrium sorption depends (although to a small extent) on the dye, the cellulose, and the salt concentration. In studying the sorption of direct dyes on viscose, Neale found that the equilibrium sorption is roughly halved by a rise in temperature of 20° C. (16) or (a later figure) 30° C. (13). In the present work it was found (Fig. 7) that at a constant dye concentration of 25 mgm. per litre the equilibrium sorption of Calcodur Blue 4GL on natural cotton yarn was approximately halved by a rise in temperature of 20° C., from 70° C. to 90° C., but that as the equilibrium dye concentration in the bath increases (at a fixed salt concentration) a greater temperature range is required in order to effect a halving of the equilibrium sorption. The temperature coefficient of the equilibrium sorption thus depends on the equilibrium concentration of dye in the bath, which statement is, of course, deducible from the finding that the value of the differential heat of sorption depends on the extent of the equilibrium sorption.

Acknowledgments

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* *With a given dye, spatial considerations may require that certain of the dye particles arriving at the surface after a measure of sorption has taken place form fewer bonds than do those arriving earlier at the fresh surface.*

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THE OCCURRENCE AND DISTRIBUTION OF *SALMONELLA* TYPES IN FOWL

II. STUDIES OF ARTIFICIAL *S. BAREILLY* AND *S. ORANIENBURG* INFECTIONS IN HENS[1]

By F. E. Chase[2]

Abstract

Experimental studies carried out on a limited number of hens infected orally with *S. bareilly* indicated that occasionally such hens may lay contaminated eggs. Using the estimated numbers of *S. bareilly* in the feces as the criterion of infection, considerable variation in susceptibility was evident, the carrier period ranging from 5 to 40 days. The organisms were recovered from the intestinal tract and in one instance from the spleen. The apparent development of resistance to repeated oral inoculation was demonstrated. Experiments of a similar nature were made with hens infected orally with *S. oranienburg*. No contaminated eggs were found, though in this case low egg production resulting from some of the hens moulting reduces the significance of this finding. Fecal counts were lower than those obtained from the *S. bareilly* infected hens. *S. bonariensis* was isolated from the feces of two hens during this experiment.

Introduction

The isolation of *Salmonella* types from Canadian dried egg powder by Gibbons and Moore (6) has served to stimulate interest in the probable source of these contaminants. There is ample evidence in the literature to show that chickens and hens may act as host to many *Salmonella* types in addition to the long recognized *S. pullorum* (9, 10), and in the case of closely related fowl, such as ducks, pigeons, and turkeys, that contaminated eggs may be produced by birds naturally infected with *Salmonella* organisms (3, 8).* It has also been demonstrated by Shalm (11) that the contents of hens' eggs may become contaminated with *Salmonella* as a result of smearing the unbroken shells with contaminated feces.

However, the expected isolation of *Salmonella* types, other than *S. pullorum* from hens' eggs, has been slow in appearing (2),** but it has been reported recently by Watt (12) in his account of a food poisoning outbreak that occurred on board ship and that was traced to the presence of *S. montevideo* in the contents of hens' eggs. Watt also described the isolation of two additional types, *S. cholerae suis* and *S. derby*, from hens' eggs. Later Gibbons (5) succeeded in isolating *Salmonella* types from eggs produced by two naturally infected flocks of hens.

A study of hens artificially infected with *S. bareilly* has been reported by Gibbons and Moore (7). Of 37 eggs laid during the period the organism was

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excreted, they found three with contaminated shells. Gauger and Greaves (4) have reported studies of a similar nature made with turkeys infected with *S. typhimurium*.

This paper deals with bacteriological studies involving two groups of hens, one infected artificially with *S. bareilly* and the other with *S. oranienburg*. Information was sought primarily on three questions: the extent to which hens infected by the oral route may lay contaminated eggs, how long they would continue to excrete the organisms in feces, and where the organisms tended to localize.

Methods

S. bareilly and *S. oranienburg* were the types selected for this study since, except for *S. pullorum*, they were found in egg powder with the greatest frequency by Gibbons and Moore (6). The cultures were obtained from Dr. N. E. Gibbons and represented strains isolated from egg powder. In all cases inoculation into the crop was made orally by the introduction, with a pipette, of 1 ml. of a 24 hr. nutrient broth culture of the organism.

The general plan of the experiments was the same for both organisms, being as follows: (*a*) bacteriological examination of shells and contents of all sound eggs obtained prior to and during the period of artificial infection; (*b*) study of duration of infection using four hens from which daily fecal samples were examined over a period of two to three months; (*c*) localization of organisms was studied using four or five hens that were inoculated and a bird sacrificed and organs examined bacteriologically at four or five day intervals; (*d*) effect of weekly inoculation was studied for a period of three to four months using one hen only.

In all, 19 Barred Rocks were used in these studies, 9 in the *S. bareilly* series and 10 in the *S. oranienburg* inoculated group. Prior to inoculation these hens were kept under observation for a period of three weeks, during which time eggs and fecal samples were examined for the presence of *Salmonella* types; in addition agglutination tests were made with *S. pullorum* antigen and an 'O' antigen of *S. bareilly* or *S. oranienburg*. In all these tests, results were negative, hence it was assumed that the hens were free from *Salmonella* infection of Group C or D types.

The number of birds under test at one time was limited to five. The first group of five hens was kept in individual cages, the floors of which were covered with clean paper each day. A large percentage of the eggs laid by this group was soiled with feces. This was done to obtain information on eggs produced under conditions of filth. The remaining hens were kept in individual cages with wire floors, the feces being collected on trays lined with paper that was changed daily. In the latter instance eggs free from gross fecal contamination were obtained.

Fecal samples were examined within a few hours of being collected with the exception of those obtained on Sundays, which were refrigerated overnight.

The numbers of *Salmonella* organisms present in the feces were estimated by means of the "Most Probable Number" (MPN) technique (7).

The eggs were collected daily and held at room temperature until examined, the holding period ranging from 0 to 20 days. The shells and contents of all eggs were examined for *Salmonella* organisms by methods previously described (2).

A post-mortem examination was made on each hen, including a study of gross appearance, and cultural and serological examinations. Cultural studies consisted of inoculation of two enrichment media, Bacto-Tetrathionate Broth and Brilliant Green Bile 2%, from the following sources: liver, gall bladder, spleen, oviduct, ovaries, two or three of the largest ova, and the contents of the duodenum, upper intestine, lower intestine, and caeca. Following incubation the broth media were streaked on Bacto-SS Agar and colourless colonies checked as described above.

Blood samples were collected when the hens were sacrificed and used in agglutination tests with 'O' antigens of the type with which the bird was inoculated.

Results

S. bareilly Experiments

To determine the duration of experimental infection four hens were inoculated (inoculum contained 990,000,000 per ml.), and fecal samples examined daily for approximately two months. The results of studies made with this group are summarized in Table I. Though three hens seemed unaffected by the inoculation, bird A-1 became morbid on the second day, refusing food and squatting in a corner of the cage, but by the fifth day had apparently recovered. Bacteriological examination of the feces did not uncover any great difference in the *S. bareilly* counts between this hen and the other three, though it carried the organisms for a shorter period. In the hope of discovering the reason for the reaction, A-1 was sacrificed on the 14th day, but no explanation was forthcoming since she appeared normal and was free of *S. bareilly* according to the cultural methods used. The fact that serological tests on this hen were negative seems to argue against the possibility that tissue invasion had occurred. This was the only hen of the entire group of 19 to show signs of illness following inoculation. Of 54 eggs laid by this group of hens during the period *S. bareilly* was being excreted, two were found with contaminated shells.

To gain information on the localization of *S. bareilly* in hens, a second group of four was inoculated (inoculum contained 940,000,000 per ml.), and a bird was sacrificed and a post-mortem examination made at intervals of approximately five days. Table II indicates the results of this experiment. In the case of A-8, it is apparent that the infection did not become established, thus explaining the failure to isolate the organism on post-mortem. *S. bareilly* was isolated from the caeca of A-7 on the fifth day, from the caeca and lower intestine of A-6 on the 10th day, and from the spleen of A-9 on the 16th day. It is suggested that the presence of *S. bareilly* in the spleen of A-9 probably explains the higher titre shown by this hen in the agglutination test.

TABLE I

EXCRETION OF *S. bareilly* BY HENS FOLLOWING ORAL INOCULATION, TOGETHER WITH RESULTS OF EGG AND POST-MORTEM STUDIES

Days since inoculation	Hen							
	A-1		A-2		A-3		A-4	
	Feces, (MPN per gram)	Egg	Feces, (MPN per gram)	Egg	Feces, (MPN per gram)	Egg	Feces, (MPN per gram)	Egg
1	0	C	0	D	<1	D	0	
2	0		3		0		92	D
3	0		0	D	5		2	
4	<1		>160	D	0	C	0	
5	1		<1		2		0	D
6	0		2	C	<1	C	>160	
7	92		24	C	<1	C	24	D
8	35		0	D	0		160	
9	2		<1		0		<1	D
10	0		0	D	2	C	<1	C
11	0		>160		>160	D	0	C
12	0		>160	C	>160		92	D
13	0		0	C	16,000		170	C
14	0		<1	D	>16,000	C	0	
15			3	D	9200		35	C
16			3	D	1600		1	D
17			0	D	1	C	1	
18			0	C	>16,000		<1	DS
19			5		3	DS	59	C
20			0	D	<1		0	D
21			3		54	D	0	
22			0	C	2		0	
23			0		0		0	
24			0	D	0	D	0	D
25			0	D	0		0	
26			2	D	>16,000		0	D
27			0	C	92	C	0	
28			0		>160	C	0	D
29			0	D	2		0	
30			0	C	0		0	
31			0		0		0	C
32			0	D	0		0	
33			0	C	>160	C	0	
34			92		0	D	0	
35			0	C	>160		0	D
36			0		0		0	
37			0	D	0		0	
38			0		0		0	
39			0	D	0		0	D
40			0		>160	C	0	D
			1		2		3	
Post-mortem								
Appearance	Normal		Normal		Normal		Normal	
S. bareilly	Not recovered		Not recovered		Not recovered		Not recovered	
Serological tests using 'O' antigen	1000*		3100		2100		3210	

Note: *C* = *Clean shell.*
D = *Soiled shell.*
S = *S. bareilly isolated from shell.*
1 = *Feces negative to the 55th day, 10 dirty eggs also negative.*
2 = *Feces negative to the 63rd day, three clean and three dirty eggs also negative.*
3 = *Feces negative to the 58th day, four clean and eight dirty eggs also negative.*
* *Serum dilutions of 1 : 20, 1 : 40, 1 : 80, and 1 : 160.*

TABLE II

LOCALIZATION OF ARTIFICIAL *S. bareilly* INFECTION IN HENS AS SHOWN BY POST-MORTEM STUDIES, TOGETHER WITH RESULTS OF FECAL AND EGG EXAMINATIONS

Days since inoculation	Hen							
	A-6		A-7		A-8		A-9	
	Feces, (MPN per gram)	Egg	Feces, (MPN per gram)	Egg	Feces, (MPN per gram)	Egg	Feces, (MPN per gram)	Egg
1	>160	C	0		>160		>160	
2	>160		24		0		>160	
3	>160		3		54		22	
4	540	C	5		0		1600	
5	9200		17		11		16,000	
6	92,000	CI			0	C	54,000	C
7	5400				0		9200	
8	490				0		490	C
9	32	C			0		5400	C
10	160				0	C	54	C
11					0	C	0	C
12					0	C	0	C
13					0	C	0	C
14					0	C	240	
15					0	C	2	
16					0	C	0	C
					1			
Post-mortem Appearance	Perforated duodenum, ruptured ovum		Haemorrhage from right kidney		Normal		Normal	
S. bareilly	Isolated from caeca, lower intestine		Isolated from caeca		Not recovered		Isolated from spleen	
Serological tests using 'O' antigen	1000*		1000		4000		4321	

Note: *C = Clean shell.*
I = S. bareilly isolated from interior.
1 = Feces negative to the 26th day, one clean egg also negative.
* *Serum dilutions of 1 : 20, 1 : 40, 1 : 80, and 1 : 160.*

It will also be seen from Table II that of 12 eggs laid by the established carriers, A-6 and A-9, *S. bareilly* was isolated from the contents of an egg laid by A-6. Since this egg was clean and was cultured the same day it was laid, there is little reason to suspect that the organism passed through the shell. On the other hand, the post-mortem examination, made four days after the egg was laid, revealed a perforated duodenum and the presence of several agglomerations of fecal material in the peritoneal cavity. This, together with the fact that *Escherichia coli* was found associated with *S. bareilly* in this egg, seems to indicate that the infection probably occurred through the infundibulum. Though the circumstances described above suggest that the perforation had occurred several days previously, there was no indication of peritonitis

at the time of autopsy, and culture of the largest clump of fecal material failed to isolate any *Salmonella*. The fact that this hen at no time displayed any sign of illness is considered of interest since it suggests a high level of resistance.

To determine the effect of repeated inoculations, A-5 received one ml. of a 24 hr. broth culture of *S. bareilly* at weekly intervals for 15 consecutive weeks. Results are shown in Table III. It will be seen that the greatest excretion of

TABLE III

EXCRETION OF *S. bareilly* BY A HEN INOCULATED ORALLY AT WEEKLY INTERVALS, TOGETHER WITH RESULTS OF EGG AND POST-MORTEM STUDIES

Hen A-5								
Days since first inoculation	Feces, (MPN per gram)	Egg	Days since first inoculation	Feces, (MPN per gram)	Egg	Days since first inoculation	Feces, (MPN per gram)	Egg
1	0	D	36	0		71	0	D
2	1		37	0		72	>160	C
3	0	D	38	0	C	73	0	
4	2	D	39	0	D	74	>160	D
5	2	C	40	1600		75	8	
6	0	C	41	0	C	76	0	D
7	<1	D	42	54	D	77	0	
8	92	C	43	35	D	78	3	D
9	>160	D	44	<1	D	79	>160	
10	>160	D	45	>160		80	>160	C
11	>160	C	46	0	D	81	0	C
12	24		47	0	C	82	>160	
13	7	D	48	0		83	160	C
14	54	D	49	0	C	84	0	C
15	>16,000	C	50	3	D	85	>160	
16	95		51	>160	D	86	22	
17	5	C	52	54	C	87	5	C
18	16,000		53	0	D	88	0	C
19	>16,000	D	54	0	D	89	3	
20	35		55	0		90	0	C
21	0		56	1	C	91	0	C
22	>160		57	0	C	92	>160	
23	2		58	>160		93	0	C
24	<1		59	>160	C	94	0	C
25	0		60	0	D	95	35	
26	92	D	61	160	DS		1	
27	11,000	C	62	<1				
28	<1		63	0	D			
						Post-mortem Appearance	Proventriculus and duodenum enlarged	
29	10		64	>160				
30	0		65	>160	D			
31	0		66	0	DI	*S. bareilly*	Not recovered	
32	0		67	0				
33	<1		68	5	D	Serological tests using 'O' antigen	4000*	
34	<1		69	35	D			
35	0		70	1	D			

Note: *C = Clean shell.*
D = Soiled shell.
I = S. bareilly isolated from interior.
S = S. bareilly isolated from shell.
1 = Except for the 99th day, feces negative to the 110th day; 10 clean eggs also negative.
* *Serum dilutions of 1 : 20, 1 : 40, 1 : 80, 1 : 160.*

S. bareilly occurred during the second or third week. In succeeding weeks there was an evident tendency toward high counts the first few days after inoculation, with *S. bareilly* appearing in low numbers or not at all the latter part of the week. Of 60 eggs obtained during the period this hen was a carrier, two yielded *S. bareilly*, in one instance from the shell and in the other from the contents. The only abnormality noticed on post-mortem examination was the enlarged and highly vascularized proventriculus and duodenum. Table III also indicates how well egg production was maintained, except for the fourth and fifth weeks; this, together with the pattern shown by the fecal counts, suggests the development of resistance to repeated oral inoculations.

S. oranienburg Experiments

To determine the duration of artificial infection, four hens were given an oral inoculation of a 24 hr. broth culture of *S. oranienburg*, containing, according to plate count, 770,000,000 organisms. Fecal samples were examined daily for approximately three months and the results are shown in a somewhat condensed form in Table IV. This group was selected from pullets that were just starting to lay, but since they began to moult soon after inoculation, egg production was very low. In all, only 27 eggs were obtained for culture following inoculation; 19 of these were laid by B-1. *S. oranienburg* was not isolated from the shell or meat of any of these eggs.

A finding of interest was the isolation of *S. bonariensis* from the feces of B-1 and B-2 on the 10th and 8th days, respectively, after inoculation with *S. oranienburg*. As far as is known to the author, this is the first evidence of the association of this organism with fowl.

Hen B-3 was sacrificed and examined on the 80th day, after a progressive illness of a week's duration. It was apparently suffering from 'big liver disease'. *S. oranienburg* was not recovered from this hen nor from the remaining three when cultured a few days later.

To study the localization of the organisms, five hens were inoculated with a broth culture that gave a plate count of 860,000,000 per ml. Daily fecal examinations yielded only two *S. oranienburg* cultures, one from B-6 on the second day and one from B-10 on the eighth day, with the MPN per gram being 23 and 5, respectively. A hen was sacrificed at four-day intervals following inoculation, but it was not surprising, in view of the results of the fecal examinations, that no cultures were obtained at autopsy. No explanation can be given for the failure to establish infection in this group, though it was noticed, during the period of observation prior to inoculation, that the intestinal flora of these birds was somewhat different from that of the hens previously studied. Six eggs laid by this group after inoculation gave negative results to cultural studies.

To determine the effect of repeated inoculations, B-5 was inoculated orally with *S. oranienburg* at weekly intervals for 12 consecutive weeks. Fecal studies indicated the same general picture as those of hen A-5 shown in Table III. Four eggs only were obtained and these were negative on cultural

TABLE IV

EXCRETION OF *S. oranienburg* BY HENS FOLLOWING ORAL INOCULATION, TOGETHER WITH RESULTS OF EGG AND POST-MORTEM STUDIES

Days since inoculation	Hen							
	B-1		B-2		B-3		B-4	
	Feces, (MPN per gram)	Egg	Feces, (MPN per gram)	Egg	Feces, (MPN per gram)	Egg	Feces, (MPN per gram)	Egg
1	>160		>160		>160	C	>160	
2	1	C	>160	C	>160		>160	
3	0	C	13	C	220	C	54	
4	92	C	0		0	C	43	
5	0	C	0	C	35		310	C
6	0		0	D	24		4	
7	0		0		0		24	
8	1600		**		0		220	
10	**		0		0		0	
15	0	C	0	C	0		0	
18	0		0		0		>160	
19	0	C	0		0		12	
20	>160	C	0		0		0	
21	0	C	0		0		0	
23	3	C	0		0		0	
24	>160	C	0		0		0	
25	50		22		0		1	
27	0	C	0		0		0	
28	35	C	0		0		0	
29	0		0		0		1	
32	0		0		0		35	
34	0		0		0		1	
35	0		0		0		2	
43	24		0		0		0	
50	81		0		0		0	
57	0		0		1		0	
62	0	C	0		0		0	
63	0	C	0		0		0	
65	0	C	0		0		1	
69	0	C	0		0		0	
71	0	C	0		0		0	
83	0		0		0		3	
84	0		0		0		3	
85	0	C	0		0		0	
87	0	C	0		0		1	
Post-mortem Appearance	Normal		Normal		'Big liver'		Ruptured ovum	
S. oranienburg	Not recovered		Not recovered		Not recovered		Not recovered	
Serological tests using 'O' antigen	4210*		3210		0000		1000	

Note: *C = Clean shell.*
D = Soiled shell.
* *Serum dilutions of 1 : 20, 1 : 40, 1 : 80, and 1 : 160.*
** *S. bonariensis isolated.*

examination. Weekly serological tests showed some variation, but the titre at no time was higher than 'one plus' at 1/80 dilution of serum in *S. oranienburg* 'O' antigen. This hen was autopsied at 90 days and was normal in appearance and negative culturally.

Discussion

It is recognized that the small number of hens employed in these experiments places a limitation on the value of the results obtained. For this reason a comparison of the results of the present study of *S. bareilly* infected hens with those of Gibbons and Moore (7), who used six hens, is of especial interest. They reported the excretion of *S. bareilly* from the intestinal tract of orally infected hens over a period of 18 to 38 days, the isolation of *S. bareilly* from the intestinal tract and liver, and also from the shells of 3 of 37 eggs laid while the organism was being excreted. It is evident that the results of the present experiments, namely, a carrier period of 5 to 40 days, the isolation of *S. bareilly* from the intestinal tract and spleen, and from the shells or contents of 5 of 124 eggs laid while the hens were carriers, show favourable agreement. The only significant difference has been the isolation of *S. bareilly* from egg contents. Of interest is the fact that the three eggs found in the present experiment with contaminated shells were classed as 'dirties' while the shells of the two with contaminated contents were clean.

With respect to the results of the *S. oranienburg* experiments, no significance can be attached to the failure to isolate the organism from the eggs because of the small number of eggs examined, and also because the low fecal counts obtained suggest a lower level of infection than that occurring in the *S. bareilly* inoculated hens. In the latter connection it is interesting to note that Edwards and Bruner (3) found the incidence of *S. oranienburg* in fowl to be approximately half that of *S. bareilly*.

Whether the intermittent isolation of *S. oranienburg* from the feces of B-1 and B-4 indicates a prolonged carrier period is open to question since B-5, receiving weekly inoculations, was carried along simultaneously, and could, therefore, conceivably have served as a source of reinfection of these hens or accidental contamination of their feces. Precautions taken against these eventualities were: the housing of B-5 in the bottom row and the other birds in the top row of a three-tier bank of cages; and the use of aseptic technique in handling the feces. As a further precaution against accidental contamination, the sample of feces from B-5 was the last to be taken each day. In addition to these possibilities, sampling error was doubtless large because no attempt was made to mix the total excretion of feces for the 24 hr. period before the samples were taken.

The fact that Gauger and Greaves (4), in their study of artificial and natural *S. typhi-murium* infection in turkeys, isolated the organism from both shell and contents of eggs laid by the former group but from the shell only in the latter instance, emphasizes the importance of securing naturally infected hens for investigations of this nature, if at all possible. Considerable effort has been expended to this end by the author, so far without success.

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THE OXIDATION, IGNITION, AND DETONATION OF FUEL VAPORS AND GASES

I. A REACTION CHAMBER ADAPTED TO DETERMINE THE EFFECT OF ANTIKNOCKS ON THE RAPID OXIDATION OF FUEL VAPOR AT HIGH TEMPERATURES[1]

By R. O. King[2]

Abstract

Slow combustion experiments by conventional laboratory methods show that metallic dopes such as the iron and nickel carbonyls and tetraethyl lead act as antioxidants in respect of the liquid paraffins present in engine fuel, the effect being especially marked at high temperatures. Such an effect failed to account for the results of certain engine experiments which could be interpreted only on the assumption that the metallic dopes *promoted* oxidation of the 'end gas' which is known to be the seat of knock.

The inconsistencies mentioned justified an investigation of conventional laboratory methods of measuring rate of oxidation. This led to the design of a small scale flow method reaction chamber in which a typical paraffin, such as pentane, containing iron carbonyl in small concentration and mixed with air in combining proportions could be oxidized to final products, without explosion, in a time of exposure of one second or less at temperatures rising to 700° C. Oxidation of the doped pentane was to the final products, carbon dioxide and steam, at all temperatures of reaction, rate of formation of carbon monoxide being barely measurable. On the other hand, the oxidation of pentane alone was accompanied by a profuse liberation of aldehyde, reaching a maximum rate at about 400° C. and giving a negative temperature coefficient of reaction over the range 400° to 500° C. Oxidation of the pentane alone occurred at a much lower rate, over the high temperature range, than when it contained iron carbonyl in the usual small proportion (½ of 1%).

The new reaction chamber was used less successfully in demonstrating the effect of tetraethyl lead to promote the oxidation of pentane owing to difficulties arising from the properties of lead. A measurable promoting effect was, nevertheless, obtained at all temperatures of reaction.

The text has been restricted to an account of the development of a novel type of reaction chamber and to oxidations of pentane necessary for the purpose. The chamber is of more general application.

Introduction

Conventional laboratory bulb or flow methods yield results for the effect of antiknock substances on the oxidation of hydrocarbons used as engine fuel that are difficult or impossible to reconcile with the behavior of the substances in the combustion space of an engine. The reacting mixture in the usual laboratory apparatus is oxidized slowly and explosion occurs generally in the temperature range 500° to 600° C., unless the tube or bulb is packed. In the engine, however, complete oxidation of the reacting mixture occurs in a small fraction of a second, and the last portion to burn, the 'end gas', is exposed to temperatures rising to 800° C., depending on the compression ratio used. It was considered that the behavior of fuels in the combustion space of an engine

[1] *Manuscript received May 16, 1947.*
Contribution from Defence Research Board, Ottawa, Canada.

[2] *Research Scientist, Naval Division, Defence Research Board, lately Director of Scientific Research and Development, Royal Canadian Navy.*

might be interpreted in terms of laboratory oxidations if a reaction chamber could be designed to operate without explosion at temperatures above 500° C. and at the same time provide for complete oxidation of fuel vapor in a time comparable with that of an engine combustion period. Experimental work was undertaken accordingly and the degree of success attained is shown by results described in Sections III and IV.

Section I

Review of Published Experimental Results

The effect of antiknocks such as tetraethyl lead and the iron and nickel carbonyls on the oxidation of hydrogen and the numerous hydrocarbon constituents of engine fuel has been studied by many investigators. Conventional 'flow' or 'bulb' methods of experiment were used and explosion of the combustible mixture undergoing oxidation occurred at temperatures ranging from 500° to 600° C. unless the oxidation space were 'packed'. A complete review of the published experimental results would be lengthy and it will suffice to mention some of the more significant.

Pope, Dykstra, and Edgar (8) using an open tube flow method found that tetraethyl lead tended to inhibit the oxidation of *n*-octane at temperatures rising to 600° C.; inflammation occurred at higher temperatures.

Berl, Heise, and Winnacker (1) using a packed oxidation space were able to observe oxidations at 500° and 700° C. They obtained a more decided antioxidant effect for both tetraethyl lead and iron carbonyl in respect of pentane and hexane and, for example, reported that "by the addition of 1% of iron carbonyl under the conditions stated, the hexane remains practically unchanged; the oxygen remains unused".

Mardles (5) using the bulb method over the temperature range 230° to 320° C. found that tetraethyl lead tended to inhibit the oxidation of hexane at temperatures above 250° C. but promoted the effect at lower temperatures, and in a later publication (6) described experiments, made with a conventional flow method, showing an oxidation promoting effect for either tetraethyl lead or iron carbonyl in respect of hydrogen, methane, and ethane, irrespective of temperature. The inversion of the effect of metallic dopes was mentioned. No explanation was offered other than the quoted opinion of Moureau and Dufraisse that certain substances may act as oxidants in respect of some compounds and as antioxidants in respect of others.

Pidgeon and Egerton (7) using the bulb method at a constant temperature of 265° C. found the oxidation of pentane to be promoted when tetraethyl lead was freshly added; an inhibitory effect was observed after the metal of the dope became oxide.

The experimental work to which reference has been made, as well as a great deal of similar work not mentioned, was initiated in an endeavor to explain the antiknock effect of metallic dopes. Knock was regarded by many as due primarily to an oxidation process beginning with the formation of explosive

organic peroxides. The metal of the dope was supposed to destroy the peroxide or, in some way rather difficult to explain, interrupt chain reactions in which peroxides were essential links. The experiments were of the slow combustion type made generally at relatively low temperatures, and it is difficult to use the results as a foundation for a rational explanation of the effect of the dopes on combustion of the end gas in an engine which goes to completion in a small fraction of a second on exposure to temperatures extending to 800° C. The results are, however, in agreement in showing that, *in the conditions in which they were obtained*, the metallic antiknocks inhibit in varying degree the oxidation of the higher paraffins present in large proportion in commonly used engine fuel and mainly responsible for fuel knock. Some doubt was, however, cast on the validity of the antioxidant effect by finding that engine experimental results, not yet described, could be explained only by assuming that the dopes *promoted* oxidation in the related conditions.

The disagreement between laboratory and engine experimental results was discussed with Dr. F. H. Garner, Chief Chemist in England of the Standard Oil Development Co., and Prof. E. K. Rideal. The discussion led to arrangements being made to undertake a series of oxidation experiments, using new methods, in the Colloid Science Laboratory, Cambridge University. The experiments are described in succeeding sections, beginning with a description of the preliminary work required to recover typical oxidation results obtained by others and to devise a reaction chamber to reproduce in some degree the temperature and 'time of exposure' conditions prevailing in the combustion space of a carburetor engine.

Section II

Preliminary Experiments and Reaction Chamber No. 10

Oxidation research is usually conducted with a particular form of a conventional method to determine the characteristics of a number of substances. Thus it seemed that whether metallic antiknocks promoted the oxidation of some substances or inhibited the effect in others or reversed in effect on increasing temperature might depend on the form or scale of the laboratory apparatus. It was decided, therefore, to depart from the usual procedure by selecting one typical liquid paraffin for all the experiments and to confine the variables to the scale and design of reaction spaces.

The flow method of experiment was selected in preference to the bulb method for two principal reasons; (1) it permitted flexibility in the design and scale of the reaction space, and (2) it enabled samples of the reaction products to be withdrawn at any temperature for analysis. The experiments were made with mixtures of pentane vapor with air. The methods of fixing 'mixture strengths', of measuring rate of mixture supply to the reaction space, and of analyzing the oxidation products are described in the appendix.

Typical Oxidation Results (Mardles) for Pentane and Hexane, Conventional Flow and Bulb Methods

The results have already been mentioned, Section I. Those for pentane obtained by Mardles (6) using the flow method are shown graphically by Fig. 1. It will be noted that oxidation begins at about 220° C. and proceeds the more rapidly in the doped mixture until the temperature reaches 400° C. The graphs then cross and at higher temperatures the pentane is oxidized more rapidly than with tetraethyl lead added. The conditions of the experiment are not stated in the text of the reference quoted but it is known that

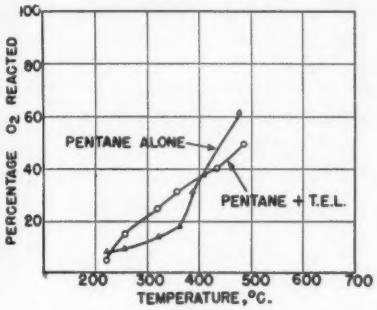


FIG. 1

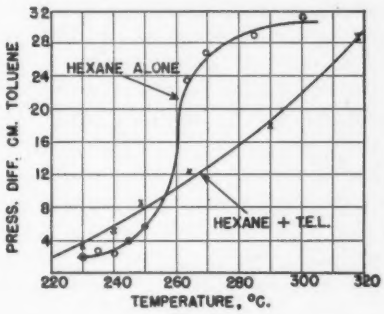


FIG. 2

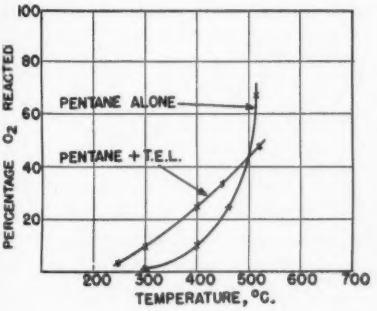


FIG. 3

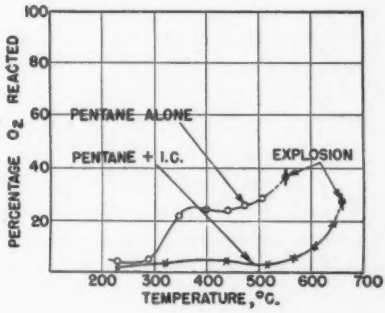


FIG. 4

FIG. 1. *Pentane oxidation (Mardles). Tube method,* $\frac{L}{D} = 25$. *Flow = 16 cc. per min.*

FIG. 2. *Hexane oxidation (Mardles). Bulb method.*

FIG. 3. *Pentane oxidation (King). Tube method,* $\frac{L}{D} = 32$. *Flow = 150 cc. per min.*

FIG. 4. *Pentane oxidation (King). Tube method,* $\frac{L}{D} = 6$. *Flow = 150 cc. per min.*

the rate of mixture supply was approximately 1 litre per hour, determined by 'counting bubbles'. The combustion tube was the usual hard glass variety, 12 mm. inside diameter supported horizontally in a tubular electric furnace 12 in. long. The mixture strength was determined by weighing a surface carburetor 'before and after'. Oxidation results obtained by Mardles (5) for

hexane, using the bulb method, are shown graphically by Fig. 2. Experimental details are given in the reference quoted. It will be noted that the reversal of the oxidation promoting effect of the tetraethyl lead is at approximately 255° C., that is, 145° C. lower than observed for the pentane oxidation.

Effect of Changing Ratio of Length to Diameter of Combustion Tube

The Cambridge experiments were begun with the conventional set up of a combustion tube in a tubular electric furnace except that the furnace was exceptionally long (24 in.), the combustion tube being of Pyrex approximately 19 mm. internal diameter. The L to D ratio was, therefore, 32 instead of 25 as used by Mardles. The results of the oxidation of pentane alone and with the small addition of 0.25% by weight of tetraethyl lead are given by the graphs of Fig. 3. Comparing them with those of Fig. 1, it will be noted that the promoting effect of tetraethyl lead at relatively low temperatures was similar to that observed by Mardles but was maintained until the temperature reached 500° C., that is, 100° C. higher. The experiments showed that the general characteristics of pentane oxidation already described in references given had been recovered. The next significant change in the reaction space was to *reduce* the L to D ratio to 6 by using a furnace 6 in. long and a combustion tube of 1.0 in. internal diameter. A Jena Supramax Glass tube was used in the expectation that it might be possible to carry oxidation to temperatures above 600° C. Temperatures were taken by a ring thermocouple of two junctions surrounding the combustion tube at the position of maximum temperature instead of by the usual arrangement of a couple enclosed in a silica sheath and fixed within the combustion space. The hot upper end of the combustion tube was closed by a stainless steel block provided with an outlet tube and surmounted by a safety cap which blew off in the event of an explosion and prevented damage. All joints were ground and remained tight.

The experimental results for pentane and pentane plus iron carbonyl oxidized in the short wide tube are given by the graphs of Fig. 4. They are quite remarkable in showing a greater *antioxidant* effect than obtained by any others in open combustion tubes—moreover, there was no reversal of the effect; it persisted from the temperature of initiation to that of explosion. Similar results were obtained when the pentane was doped with tetraethyl lead. It will be noted that the explosion temperature increased over 100° C. on adding the antiknock compound to the pentane although rate of reaction *diminished.* It is also noteworthy that with the relatively large diameter tube a 'hump' showing a slight negative temperature coefficient of reaction appears in the graph for the oxidation of pentane undoped. Similar results were obtained when combustion tubes of the same L/D but of different materials were used. The materials tried were nickel-steel, silica, and graphite.

The experiments seemed to have come to a dead end with an exceptionally complete verification of the antioxidant effect of tetraethyl lead in respect of a typical liquid paraffin and consequent confirmation of current theory that the antiknock effect is obtained accordingly. It was evident that if the

metallic antiknocks promoted oxidation at high temperatures, as seemed to be indicated by engine experiments, the effect could not be demonstrated by the use of conventional bulb or tube methods, and experiments were begun to design a new type of reaction chamber.

Considerations Leading to the Development of a New Type of Reaction Chamber

It is well known that deposits of metal and various metallic oxides remain on the interior surfaces of combustion tubes after oxidations of doped vapor mixtures. It is difficult to examine the residues in long narrow tubes. Short wide tubes possess the advantage that the deposit can readily be inspected and the nature of that seen at any position related to the corresponding temperature. Moreover, there were in short tubes, when heated, very steep temperature gradients from the middle to the ends, and if the tube were used in a vertical furnace, the deposits were left in fairly distinct successive bands of metal and colored oxides on cooling the furnace and stopping the flow of doped mixture. It was observed for all the short tubes used for the experiments mentioned above that after high temperature oxidations of pentane containing tetraethyl lead or iron carbonyl a metallic mirror, as a band, remained at or near the position of entry of the tube into the furnace. It seemed, therefore, that little if any of the metal yielded by the dope reached the position of maximum tube temperature if that were much above the temperature of decomposition.

Callendar's experiments (2, 3) with organometallic compounds in sealed tubes showed that the decomposition of tetraethyl lead was nearly complete at 215° C. and left a metallic mirror on the surface of the tube. Nickel carbonyl vapor decomposed readily at 150° C., the nickel being deposited on any available surface. Decomposition occurred solely on surfaces, not in the body of the vapor. The characteristic was, in fact, discovered by Mond many years earlier and remains the basis of the commercial method used to procure pure nickel. Callendar's experiments indicate that tetraethyl lead or iron carbonyl vapor when mixed with air and fuel vapor and passed through a heated combustion tube would not reach the seat of a high temperature reaction before being decomposed at a lower temperature to yield metal which would be deposited on contact surfaces and oxidize rapidly in the conditions.

In accordance with the above mentioned considerations, experiments were made to determine the position of iron carbonyl decomposition in a 1 in. diameter Pyrex tube set horizontally in a 6 in. tubular furnace. A pentane–air mixture in combining proportion was passed into the tube at the rate of 150 cc. per min. through a 6 mm. Pyrex inlet tube as shown by Fig. 5. The pentane contained iron carbonyl in the concentration of 0.5%. The reacting mixture was allowed to flow for two hours while the temperature indicated by a ring thermocouple surrounding the tube at the middle of the furnace was maintained at 400° C. The tube was used in the horizontal position because the deposits of metal and oxides give a better indication of the path of the mixture than when the tube is vertical and the deposits appear as bands.

The traces remaining on the tube on completion of the experiment were photographed and are shown in elevation and plan by *A* and *B*, Fig. 5. They indicate the path of the mixture in the tube to be as shown by *C* of the same figure. The entering mixture, being relatively cool, falls in a stream and leaves a small iron mirror where it strikes the bottom surface. It is then heated by contact with the glass and rises through the relatively cool mixture in the entrance end of the tube, the rising stream being divided by the small mixture admission tube on which deposits of red oxide are left. The stream then strikes the top of the tube receiving more heat and moves toward the middle. The markings show, however, that it falls away from the top surface, presumably when it reaches mixture of higher temperature and consequently lower density.

It appears that when gaseous mixtures at room temperatures are admitted to the cool end of a combustion tube a heating eddy is formed. Similarly a cooling eddy is formed when the mixture leaves through a central outlet.

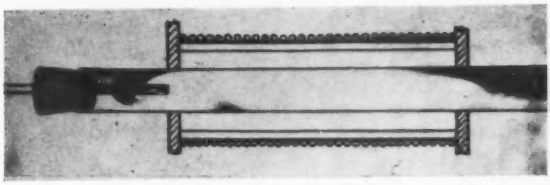
Except for the small iron mirror already mentioned, all the deposits from the eddy in the entrance end were red oxide and apparently nothing but that substance passed through the middle part, which is the position of maximum temperature and generally assumed to be that of the greatest degree of oxidation activity. That it did pass through was shown by the heavy deposit of oxide from the exit eddy.

The experiment was of general interest in showing that 'exposure time' as usually calculated is in error, but the point of immediate interest was the demonstration that the metal of the dope in a gaseous mixture passed through a conventional type of combustion tube tends to be deposited on surfaces at or near the entrance of the heating furnace as the temperature is raised. The deposition would be expected to increase with the magnitude of the entrance eddy, which in turn increases with increase in the tube diameter or a decrease in L to D ratio. Thus an explanation is afforded for the experimental results of Figs. 1, 3, and 4, showing that the antioxidant effect of the dope increases as the L to D ratio of the combustion tube diminishes. Obviously the effect of metallic dope on oxidation, as observed in engine experiments, would be reproduced in laboratory experiments only if the dope were introduced into the actual reaction space before being decomposed. The experiment showed very definitely that this condition cannot be met with the conventional straight-through combustion tube arrangement.

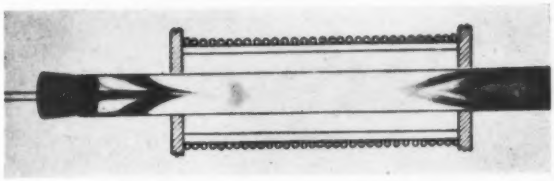
Reaction Chamber No. 10

The problem of designing a reaction chamber suitable for ensuring that the metal yielded on the decomposition of the dope content of pentane is present at the position of a high temperature reaction in a pentane–air mixture was not easy of solution. Reasonable finality of design was achieved with Reaction Chamber No. 10, illustrated by Fig. 6, *A* and *B*. *A* shows the complete arrangement as set up in an electric furnace and *B* an enlarged section of the reaction chamber and adjacent parts.

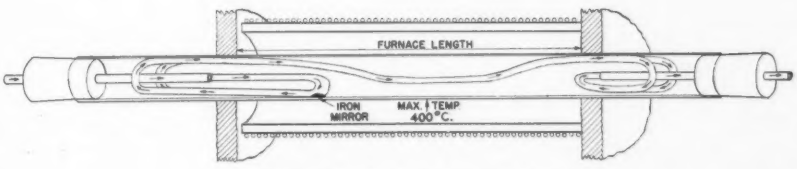
PLATE I



A. Side view of combustion tube.



B. Plan view of combustion tube.



C. Indicated path of a filament of the mixture.

FIG. 5. *Showing the effect of heat convection on the flow path of a doped pentane–air mixture through a conventional combustion tube and the very small area on which metal is deposited as a mirror.*

It will be seen by reference to the figure that the reaction chamber is an inverted cup formed in the end of a tube which is contained within another of sufficiently large diameter to provide an annulus about 1.0 mm. wide for the escape of gas from the reaction space. The tubes may be of any material suitable for use at high temperatures, provided the decomposition and oxidation products of metallic dope will adhere to the heated surfaces. The lower end of the cup is nearly closed by an asbestos cement washer, fitting closely

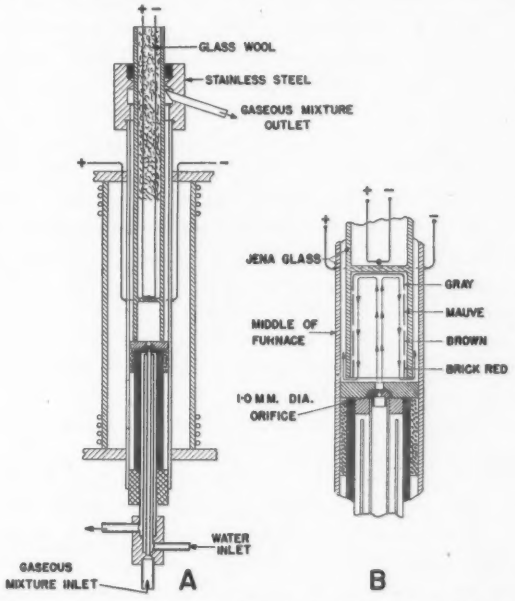


FIG. 6. *General arrangement of Reaction Chamber No. 10 in electric furnace and enlarged section of chamber.*

in the outer tube and having a small central hole through which the gaseous reacting mixture is admitted as a jet from a small orifice in the top of a water cooled inlet device. It is important that the opening from the reaction chamber into the annulus should be no greater than required to avoid appreciable resistance to the gas flow. The orifice was usually 1.0 mm. diameter but must be of such a size that the jet created by the mixture passing through it will maintain a streamline form until it strikes the top of the reaction chamber; preliminary experiment showed that in the circumstances metallic dope in the reacting mixture does not decompose until contact is made with the surface. The arrows, Fig. 6, *B*, show the path of the reacting mixture from the admission orifice, through the reaction chamber to the annulus and thence upward to the outlet tube at the upper end of the apparatus.

The reaction chamber as used for most of the experiments was 12 mm. diameter and 22 mm. long, the volume being 2.5 cc. The reacting mixture

was generally supplied at the rate of 150 cc. per minute, that is, sufficient to fill the chamber 60 times per minute. The reaction space of a four stroke internal combustion engine is filled at the same rate when the speed is 120 r.p.m.

The reaction chamber was supported in an electric furnace and thermocouples for temperature measurement arranged as shown by the diagrams, Fig. 6. A pair of thermocouples made up of a wire ring, half iron and half constantan, giving junctions at opposite ends of a diameter, was used to measure 'outside' or furnace temperature. The ring fitted easily over the outer glass tube and the connections leading to an indicator are shown by the figure. A single thermocouple was used to measure the 'inside' temperature on the top of the reaction chamber. The thermocouples and the related indicators were supplied by the Cambridge Instrument Company.

Jena Supramax glass reaction chambers were used for determining the effect of iron carbonyl on the oxidation of pentane. This variety of glass remains hard at temperatures exceeding 700° C. and resists attack by metallic oxides at lower temperatures. Decomposition and oxidation products of the carbonyl do not adhere to the glass until after a doped pentane–air mixture has been passed through the chamber for a short time while the temperature is maintained at about 700° C. The preliminary treatment effects a slight roughening of the glass. The chamber cannot properly be used for pentane oxidations after use with mixtures containing dope unless it is cleaned with hydrofluoric acid and washed with steam.

The device for ensuring that unheated doped pentane–air mixture entered the reaction chamber is shown at *A* and *B*, Fig. 6. The device was, of course, a cold body with the upper part adjacent to the high temperature reaction chamber and it was necessary to insulate it as thoroughly as possible. The insulation comprised the asbestos cement washer already mentioned and, in addition, the body of the device was wrapped with layers of asbestos paper and the upper part wound with asbestos yarn to form a plug fitting tightly in the outer tube. The insulation arrangements are illustrated by *B*, Fig. 6. The water cooled inlet device may have caused some cooling of the lower end of the reaction chamber, but at least partial compensation was obtained by adjusting the apparatus in the furnace to bring the top of the reaction chamber slightly above the position of maximum temperature. The diagram *A*, Fig. 6, is in error in showing the chamber below the position of maximum temperature. In any event, reacting mixtures, passed through the chamber at much higher rates than generally used for laboratory experiments, could be raised to the temperatures, about 700° C., required for complete oxidation.

The upper ends of the tubes of the reaction chamber became extremely hot when oxidation temperatures ran to 700° C. Rubber connections could not be used, and a special device illustrated by *A*, Fig. 6, was found to be satisfactory. The upper end of the outer glass tube was ground flat and made a joint on a flat surface of the stainless steel block. The inner glass tube passed through the block, in which a recess in the nature of a 'stuffing box' was turned. The recess was packed with asbestos.

Section III

Trials of Reaction Chamber No. 10

A combining proportions mixture of air with pentane containing iron carbonyl in the concentration of 0.5% by volume was supplied to the chamber at the rate of 150 cc. per min. and samples of oxidation products taken for analysis while the temperature was raised by steps to 700° C. The upper graph of Fig. 7 shows the rate of oxygen reacted plotted against temperature.

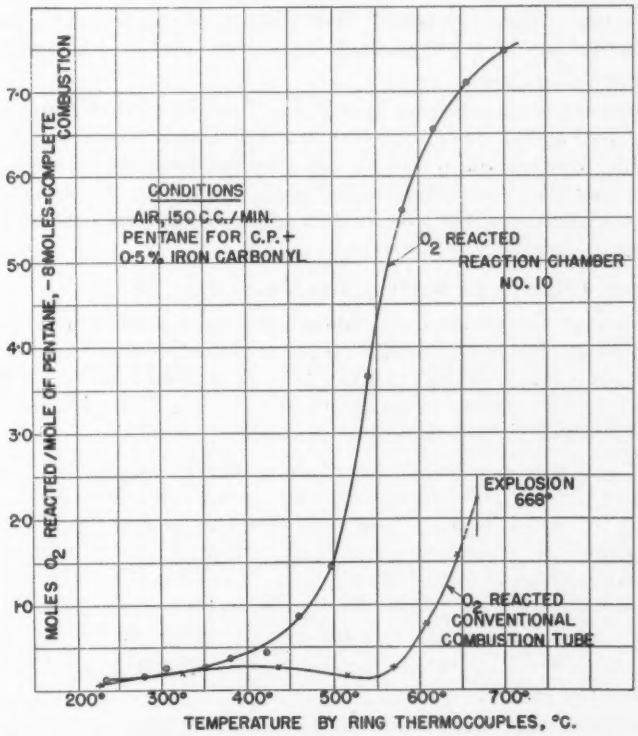


FIG. 7. *Rate of oxidation of a doped pentane–air mixture in Reaction Chamber No. 10 compared with the rate in a conventional combustion tube.*

The lower graph of the figure shows the rate at which oxygen was reacted when a similar mixture was passed through a conventional open combustion tube, 25.0 mm. diameter in a 6 in. furnace, at the rate of 150 cc. per min., as described in Section II with reference to Fig. 4.

The design of the reaction space constituted the sole difference between the conditions of the two experiments but the oxidation results differed in a somewhat remarkable manner, thus, (*a*) oxidation in Reaction Chamber No. 10 occurred at an extremely high rate especially at temperatures above 500° C.

At 600° C. the rate was 6.2 moles of oxygen reacted as compared with 0.7 moles in the conventional combustion space having a volume 30 times greater if the length of tube inside the furnace is as usual regarded as reaction space, (*b*) the doped mixture did not explode in Reaction Chamber No. 10 in spite of the high rate of reaction, reaching substantial completion at 700° C. On the other hand a similar mixture in the combustion tube exploded at about 668° C. and the last sample taken before the event showed that only 1.6 moles of oxygen had reacted. Rates of oxygen reacted, and of carbon oxides formed, in Reaction Chamber No. 10 are shown by the graphs of Fig. 8. It will be noted that carbon monoxide formation was inappreciable, indicating that oxidation was to the final products, carbon dioxide and steam, at all temperatures of reaction.

The colors of the deposits on the surface of the Reaction Chamber were as shown at *B*, Fig. 6. They appeared in distinct bands beginning with gray (iron) which covered the top of the chamber and extended a short distance down the wall, then mauve, brown, and finally brick red. The colors show the progress of oxidation of the iron in the carbonyl as it passes from the top to the bottom of the reaction chamber.

Oxidation of Pentane (Undoped) in Reaction Chamber No. 10

The pentane–air mixture in combining proportions failed to explode when passed through the chamber although the temperature was raised to 660° C. The mixture was supplied as before at the rate of 150 cc. per min. The rates of oxygen reacted are given by Graph *A* of Fig. 9. Graph *B* for doped pentane, reproduced from Fig. 7, is shown for comparison.

It will be seen by reference to the graphs that the pentane alone is oxidized at a greater rate than when doped, over the temperature range 330° to 500° C. This is the temperature range of aldehyde formation and the graph shows what became known in subsequent work as the 'aldehyde hump' with a marked *negative* temperature coefficient of reaction. The rates of formation of carbon oxides are shown by the graphs of Fig. 10 and are significant of aldehyde formation. It is of interest to compare them with the graphs of Fig. 8, which show an almost complete absence of carbon monoxide in the oxidation products of the doped pentane.

The temperature region above 500° C. is of special interest because one of the objects of the investigation was to provide means for working in the temperature range of the 'end gas' in an engine. The very great effect of the carbonyl to promote oxidation at high temperatures will be noted. Thus, referring to Fig. 9, at 600° C. with 0.5% of iron carbonyl in the pentane, 6.2 moles of oxygen were reacted to form carbon dioxide and steam whereas without the carbonyl only 1.4 moles of oxygen were reacted and oxidation was not to final products.

Inside and Outside Temperatures

The ring thermocouples surrounding the outer tube of the reaction chamber would be expected to indicate a higher temperature than the couple resting on

the top of the reaction chamber and indicating more nearly the temperature of the chamber. Outside temperatures were, however, used for plotting results, merely to continue the practice begun before the development of a separate reaction chamber within an outer tube.

When pentane alone was oxidized in the chamber, outside temperature was the higher by 17° C. at the beginning of the experiment. The difference reached a maximum of 25° C. at reaction temperatures of about 500° C. and then diminished to again become 17° C. at 600° C. The initial difference was again about 17° C. in the experiment with doped pentane, as would be expected. A maximum difference of 20° C. occurred at 400° C. and thereafter diminished to become 13° C. only at 700° C.

The inside thermocouple rested on the top surface of the reaction chamber and the temperature differences given are consistent with the view that reaction occurred mainly on the upper surface of the chamber. The temperature differences show that the rate of heat liberation was the greater when doped pentane was oxidized, as would be expected.

Section IV

Oxidation of Pentane Doped with Tetraethyl Lead in Reaction Chamber No. 10

It is evident from the experiments described in Sections II and III that the rapid oxidation in Reaction Chamber No. 10, of pentane doped with iron carbonyl, was a surface effect probably occurring mainly on iron deposited on decomposition of the carbonyl. The iron so obtained covered a considerable part of the reaction chamber surface as shown at *B*, Fig. 6, and mentioned earlier. An equal area of metal would not be expected when using lead dope because the surface of the chamber must be heated to a temperature far above the melting point of lead (327° C.) if the pentane is to be oxidized at an appreciable rate. Moreover, lead oxidizes with great rapidity in the conditions and the oxides tend to dissolve in glass at high temperatures. Thus after passing a pentane–air mixture doped with tetraethyl lead through the glass reaction chamber at high temperatures the wall surface remained smooth but discolored. There was, however, on the top surface a slight metal coating in the form of a disk about 4.0 mm. diameter covering the spot where the jet of cool reacting mixture impinged. The disk was surrounded by a ring of orange colored oxide about 1.0 mm. wide. Beyond it was a wider ring of light yellow grading off to chalk white. Similar deposits were procured in some quantity from other experiments and the chalk white substance identified as a lead oxycarbonate, $PbO.2PbCO_3$. The yellow color indicated that some PbO remained in the oxycarbonate.

In spite of the difficulties it was possible by using a steel reaction chamber to obtain conditions in which tetraethyl lead acted to promote the oxidation of pentane at temperatures ranging to 650° C., although the effect was much smaller than observed for iron carbonyl, as would be expected in view of the

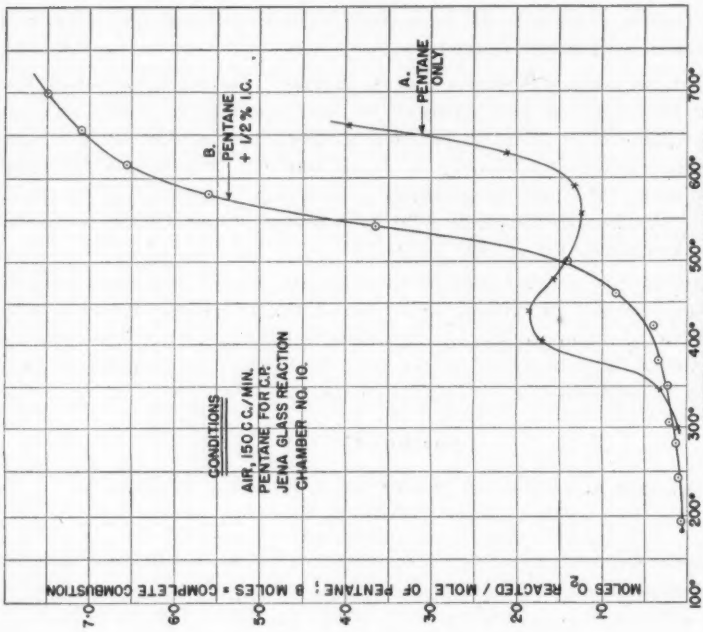


FIG. 9

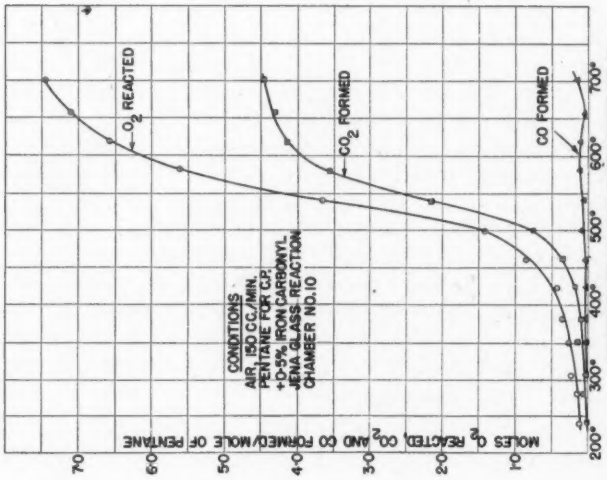


FIG. 8

FIG. 8. *Rates of carbon monoxide and carbon dioxide formation when doped pentane is oxidized in Reaction Chamber No. 10.*
FIG. 9. *The effect of iron carbonyl on the oxidation of pentane in Reaction Chamber No. 10.*

...ing effect of iron carbonyl on the oxidation of pentane in Reaction Chamber No. 10.

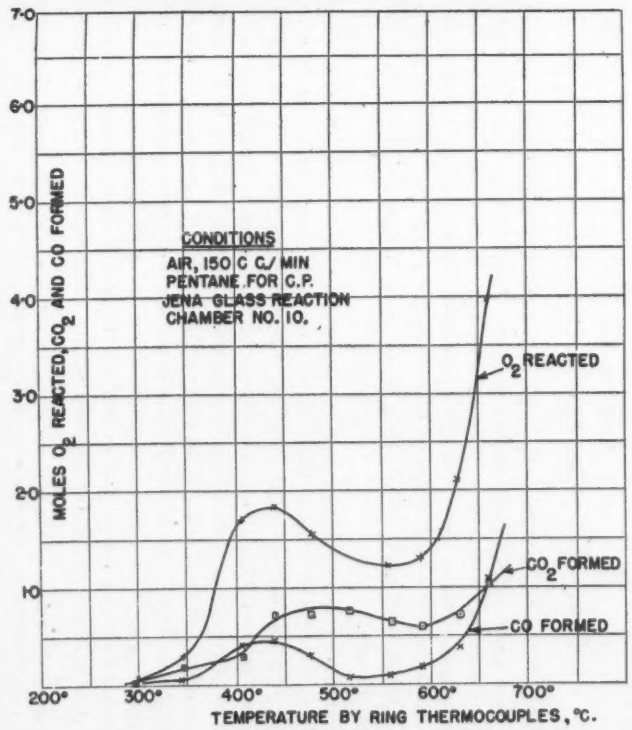


FIG. 10

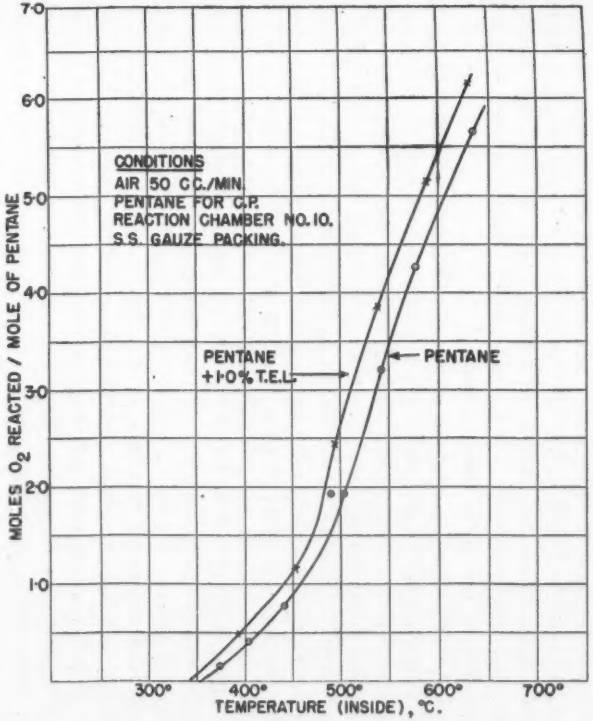


FIG. 11

FIG. 10. *Rates of carbon monoxide and carbon dioxide formation when pentane (undoped) is oxidized in Reaction Chamber No. 10.*
FIG. 11. *Effect of tetraethyl lead on the oxidation of pentane in Reaction Chamber No. 10 (packed)*

circumstances mentioned. The design was similar to that of the Jena glass chamber illustrated by Fig. 5, but a roll of stainless steel gauze was placed in the reaction space to increase the area of surface on which deposition of metal from the dope might occur. The jet of entering mixture passed into and through a central hole in the roll of gauze.

The results of oxidations of pentane alone and pentane containing tetraethyl lead in the concentration of 1.0% are given by the graphs of Fig. 11. Temperatures are as given by an 'inside' thermocouple because the 'ring' thermocouples could not be used in contact with a steel tube. Referring to the graphs it will be noted that the 'aldehyde hump' with a negative temperature coefficient of reaction has disappeared and that rate of reaction is the higher for the doped pentane at all temperatures to 650° C. with 75% of the oxygen reacted. At the temperature of 500° C. rate of oxygen reacted increased from 1.8 to 2.6 moles (44%) on the addition of the dope—the difference remained fairly constant as the temperature increased to 650° C. The oxidation promoting effect of the tetraethyl lead over the high temperature range is of special interest because it is the opposite to that obtained in conventional combustion tubes. The reacting mixture was supplied to the reaction chamber at the rate of 50 cc. per min., so moles of oxygen reacted represent a lower rate of reaction than when the rate of supply was 150 cc. per min. as for the iron carbonyl experiments. The lower rate of reaction and the lack of an aldehyde hump are attributed to the effect of packing the reaction chamber.

Section V

Review of the Experimental Results

Although the temperature and time of exposure conditions in an engine combustion space are approached in Reaction Chamber No. 10, an important other condition is not obtained. Thus the end gas in the engine is raised to an extremely high temperature* by compression while contained by relatively cool walls, except for the exhaust valve surface, but the mixture passing through Reaction Chamber No. 10 is raised in temperature by contact with the heated walls.

The metal deposited on the relatively cool walls of the engine cylinder could persist as such for a longer time in an oxidizing atmosphere than when deposited on the hot walls of Reaction Chamber No. 10. This feature is illustrated by the difficulty of maintaining lead as compared with iron on the surface of the reaction chamber. The catalytic activity of any metal coating would, however, be expected to increase with rise in temperature. Thus the upper graph of Fig. 7, for the oxidation of pentane doped with iron carbonyl, shows a gradually increasing rate of oxidation as the temperature rises from 200° C., but over the range 500° to 580° C. the rate increased from 1.5 to 5.6 moles, that is, about 400% for a rise of 80° C. The rate of change of reaction

** It is calculated from reliable indicator diagrams that when combustion is 90% complete in an engine, the temperature of the remaining unburnt mixture (end gas) has been raised by compression to 670° C. when the compression ratio is 4 to 1, and to 800° C. when it is 8 to 1.*

was in fact so great, as indicated by the slope of the graph, that a reliable observation at 540° C. was obtained only after very careful stabilization of temperature and other conditions. The rate of change of oxidation diminishes over the temperature range above 580° C. merely because reaction tends tocompletion.

The experiments with Reaction Chamber No. 10 indicate that the oxidation of doped pentane is a heterogeneous reaction. If, contrary to accepted theory, the oxidation of pentane occurs similarly, aldehyde formation depending merely on the nature of the contact surface, a simple fundamental explanation would become available for all the phenomena associated with the effect of metallic dopes on combustion in the engine. It is hoped that experiments made accordingly can be described in a subsequent publication.

Acknowledgments

The experimental work described in this paper is part only of that carried out in the Colloid Science Laboratory, Cambridge, with the co-operation of Prof. E. K. Rideal and Dr. F. H. Garner.

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Dr. E. W. R. Steacie and Dr. L. Marion, both of the National Research Council, have assisted by reading text and advising accordingly.

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APPENDIX

Methods of Measurement

Extended experimental work on oxidation, using a flow method, requires analyses of hundreds of gas samples and convenient methods of supplying reacting mixtures of known composition at known rates. The methods used for the experiments of Sections II to IV will be described briefly in order to indicate that measurements were made with sufficient accuracy; a detailed description is unnecessary for present purposes and would require separate publication.

Gas Analysis

When pentane–air mixtures flowing through a conventional combustion tube are raised to high temperatures, such oxidation as may be obtained is

accompanied by the liberation of clouds of smoke, indicating that the gas issuing from the reaction space would contain some products of decomposition such as methane, hydrogen, and unsaturateds as well as those desired, namely, products of oxidation. A complete analysis would, therefore, be tedious and difficult. When, however, similar mixtures were passed through Reaction Chamber No. 10, oxidation generally occurred with great velocity at high temperatures and the course of the reaction could then be followed by determinations of oxygen reacted, and of carbon monoxide and carbon dioxide formed, using an Ambler gas analysis apparatus.

Gas Samples:—The gases from the reaction chamber were passed through at least two condensers, the first cooled by water–ice and the second by solid carbon dioxide in acetone. The uncondensed gas could then, in the absence of appreciable pyrolysis, be assumed to contain only nitrogen, oxygen, and carbon oxides. Samples enough for two analyses were taken in 15 cc. test tubes by mercury displacement and the tubes transferred while still in the mercury trough to individual 10 cc. crucibles and stored in racks.

'Pentane' and Combining Proportions Mixtures:—The pentane, supplied by the Anglo-American Oil Company, was procured by fractional distillation from aromatic free petroleum spirit; distillation range 30° to 40° C., 60% being recovered below 33.5° C. The molecular composition was taken to be C_5H_{12} and, assuming that air contains 20.9% of oxygen, the combining proportions mixture as admitted to the reaction chamber contains the gases in the proportion of 1 mole of pentane to 8 moles of oxygen to 30.3 moles of nitrogen. The accuracy of analysis depends on the proportion of nitrogen in the reacting mixture being known and if the reacting mixture contains oxygen and pentane in correct combining proportions, then when oxidation is *complete*, nitrogen and carbon dioxide only should be found in the gas collected from the condenser, a result which was sometimes achieved.

Air Supply:—The air supply was obtained from the usual high pressure storage cylinders and was, therefore, nearly dry. The air discharged through two-stage regulators (British Oxygen Co.) and any desired rate of flow could be kept nearly constant. The air passed from the regulator through long glass capillary tubing and rate of flow was determined by pressure difference, the capillaries being calibrated *in situ* by the displacement method.

Pentane Supply:—Pentane was required at a small constant rate. The rate is 0.470 gm. per hr. for a combining proportions mixture with air at 20° C. supplied at the rate of 100 cc. per min. The pentane was supplied at any desired rate by a Rideal microdoser (4).

Carburetor:—The very simplest form only is required, especially with the more volatile fuels. The carburetor used for the experiments is illustrated, reference (4), and to ensure thorough mixing of the air and pentane vapor a length of about 3 ft. of $\frac{1}{4}$ in. diameter glass tubing was interposed between the carburetor and the reaction chamber.